Metal Imidazolate Films for Lithography Applications

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Advancements in lithography have focused on shorter exposure wavelengths and new resist types to enable finer feature patterning, resulting in denser integrated circuits and more efficient chips. However, current resist technologies may not meet future demands outlined in technology roadmaps for sub-nanometer nodes, which target features down to 5 nm and below. We introduced a class of amorphous metal organic frameworks (amorphous zeolitic imidazolate frameworks: aZIFs) as resists for electron-beam lithography (EBL), extreme ultraviolet lithography (EUVL: 13.5 nm), as well as for lithography using smaller wavelengths, beyond EUV (BEUV: 6.7 nm). The sensitivity and tone (negative or positive) of aZIFs can be tuned by the choice of metal and imidazole, and by the selection of appropriate vapor or liquid development methods. aZIF resists can be deposited by ALD/MLD, as well as by spin-on methods, with excellent control of compositions, thickness, and wafer-scale uniformity. In this talk, I will focus on negative- and positive-tone aZIF resists deposited by a spin-on method, and developed via wet and dry methods.

Although solvent-free methods hold advantages compared to liquid phase resist deposition, they also face challenges at early stage of development when facile exploration of a wide range of resist composition is desirable. Chemical Liquid Deposition (CLD) is a hybrid deposition method developed to bridge the gap between liquid-phase resist deposition (e.g., spin coating) and vacuum-based techniques (e.g., ALD/MLD). It is specifically designed to facilitate the rapid, early-stage exploration of a wide range of resist compositions, particularly metal and imidazole variations, which can be difficult to manage with purely solvent-free or traditional liquid methods. The first results from this effort have been published [1].

First, we developed a continuous laminar flow coating method using a 3D-printed microreactor for the chemical liquid deposition (CLD) of aZIF films. This method enables the creation of smooth, continuous films from ultradilute precursor solutions with controlled thicknesses ranging from a few to several hundred nanometers. The process involves mixing metal and imidazole ligand precursors in a few-second-residence-time zone to create stable, non-aggregated sol. The microreactor's engineered flow field allowed us to quantitatively analyze aZIF film deposition and develop a reaction-diffusion model that accurately describes the steady-state CLD process. This model was subsequently utilized in a computational fluid dynamics (CFD) simulation to optimize spin coating conditions for uniform film deposition. The versatility of this CLD method was demonstrated by producing various aZIF compositions, including Zn-benzimidazole (aZIF-Zn/BIm), Zn-4,5-dichloroimidazole (aZIF-Zn/dcIm), and Co-2mIm (aZIF-Co/2mIm). Furthermore, we established the application of these aZIF materials as a flexible resist platform: aZIF-Zn/2mIm acts as a vapor-phase-developed negative-tone resist, while aZIF-Zn/dcIm serves as a high-sensitivity liquid-phase-developed positive-tone resist for electron beam lithography (EBL). Preliminary results utilizing beyond EUV (BEUV) exposure further demonstrate the viability of these CLD-fabricated aZIF films for advanced, high-resolution lithographic applications.

[1] Nature Chemical Engineering 2, 594-607 (2025) Miao Y., Zheng S., Waltz K.E., Ahmad M., Zhou X., Zhou Y., Wang H., Boscoboinik J.A., Liu, Q. Agrawal K.V., Kostko O., Zhuang L., Tsapatsis M. *Spin-on Deposition of Amorphous Zeolitic Imidazolate Framework Films for Lithography Applications* https://doi.org/10.1038/s44286-025-00273-z